

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

with the file reference 103 57 315.1

filed on 05 December 2003

in the name of Covion Organic Semiconductors GmbH, Frankfurt, Germany,

and in the matter of an application for a United States Patent.

I, Dr. Ashwood Stephen DRANE, B.Sc., Ph.D., BDÜ, translator to SD Translations Ltd. of Beechwood, Chivery, Tring, Hertfordshire, HP23 6LD, England, do solemnly and sincerely declare:

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 6th day of August 2009



Dr. Ashwood Stephen Drane

FEDERAL REPUBLIC OF GERMANY



Priority certificate regarding the filing of a patent application

File reference: 103 57 315.1

Date of filing: 05 December 2003

Applicant/proprietor: Covion Organic Semiconductors GmbH,
65929 Frankfurt/DE

Title: Organic electroluminescent element

IPC: H 01 L, C 09 K

**The attached pages are a correct and accurate reproduction of the
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German Patent and Trademark Office
On behalf of
The President

[signature]

Brosig

Description

6 Organic electroluminescent element

The present invention describes a novel design principle for organic electroluminescent elements and the use thereof in displays based thereon.

10 In a number of applications of different types which can be ascribed to the electronics industry in the broadest sense, the use of organic semiconductors as active components (= functional materials) has been reality for some time or is expected in the near future.

15 Thus, light-sensitive organic materials (for example phthalocyanines) and organic charge-transport materials (generally hole transporters based on triarylamine) have already been used for many years in photocopiers.

20 The use of specific semiconducting organic compounds, some of which are also capable of the emission of light in the visible spectral region is just at the beginning of the market introduction, for example in organic electroluminescent devices. The individual components thereof, the organic light-emitting diodes (OLEDs), have a very broad range of applications as:

- 25 1. white or coloured backlighting for monochromatic or multicoloured display elements (such as, for example, in calculators, mobile telephones and other portable applications),
2. large-area displays (such as, for example, traffic signs, placards and other applications),
3. illumination elements in all colours and shapes,
4. monochromatic or full-colour passive matrix displays for portable applications (such as, for example, mobile telephones, PDAs, camcorders and other applications),
- 30 5. full-colour, large-area, high-resolution active matrix displays for a very wide variety of applications (such as, for example, mobile telephones, PDAs, laptops, televisions and other applications).

For devices containing relatively simple OLEDs, the market introduction has already taken place, as confirmed by the car radios from Pioneer that are available on the market, the mobile telephones from Pioneer and SNMD or a digital camera from Kodak with an "organic display". Further products of this type are just about to be introduced. Nevertheless, significant improvements are still necessary here in order to make these displays a true competitor to the liquid-crystal displays (LCDs) which currently dominate the market, or to surpass them.

A development in this respect which has emerged in recent years is the use of organometallic complexes which exhibit phosphorescence instead of fluorescence [M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Applied Physics Letters, **1999**, 75, 4-6].

For quantum-mechanical reasons, an up to four-fold quantum, energy and power efficiency is possible using organometallic compounds. Whether this new development will become established is on the one hand highly dependent on whether it is possible to find corresponding device compositions which are also able to implement these advantages (triplet emission = phosphorescence compared with singlet emission = fluorescence) in the OLEDs. It is not only the development of the organometallic compounds themselves that is of importance here, but also, in particular, of further materials specifically required for this purpose, such as, for example, so-called matrix or also hole-blocking materials. Essential conditions that may be mentioned here for practical use are, in particular, a long operating lifetime, high stability to thermal stresses and a low use and operating voltage together with high power efficiency, in order to facilitate mobile applications.

An organic electroluminescent device usually consists of a plurality of layers which are applied to one another by means of vacuum methods or various printing methods. For phosphorescent organic electroluminescent devices, these layers are in detail:

- 30 1. A support plate = substrate (usually glass or plastic sheet).
2. A transparent anode (usually indium-tin oxide, ITO).

- 5
3. A hole-injection layer (HIL): for example based on copper phthalocyanine (CuPc) or conductive polymers, such as polyaniline (PANI) or polythiophene derivatives (such as PEDOT).
 4. One or more hole-transport layers (HTL): usually based on triarylamine derivatives, for example 4,4',4''-tris(N-1-naphthyl)N-phenylamino)triphenylamine (NaphDATA) as the first layer and N,N'-di(naphth-1-yl)-N,N'-diphenylbenzidine (NPB) as the second hole-transport layer.
 5. One or more emission layers (EML): usually consists of matrix materials, such as, for example, 4,4'-bis(carbazol-9-yl)biphenyl (CBP), doped with phosphorescent dyes, for example tris(phenylpyridyl)iridium ($\text{Ir}(\text{PPy})_3$) or tris(2-benzothienylpyridyl)iridium ($\text{Ir}(\text{BTP})_3$). However, the emission layer may also consist of polymers, mixtures of polymers, mixtures of polymers and low-molecular-weight compounds or mixtures of various low-molecular-weight compounds.
 6. A hole-blocking layer (HBL): it usually consists of BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline = bathocuproin) or bis(2-methyl-8-quinolinolato)-4-(phenylphenolato)-aluminium(III) (BAIq).
 7. An electron-transport layer (ETL): in the majority of cases based on aluminium tris-8-hydroxyquinolinate (AlQ_3).
 8. An electron-injection layer (EIL) (also sometimes known as insulator layer (ISL)): a thin layer consisting of a material having a high dielectric constant, such as, for example, LiF , Li_2O , BaF_2 , MgO , NaF .
 9. A cathode: in general metals, metal combinations or metal alloys with a low work function, for example Ca, Ba, Cs, Mg, Al, In, Mg/Ag, are used here.

20

This entire device is appropriately (depending on the application) structured, provided with contacts and finally also hermetically sealed, since the lifetime of such devices is generally drastically shortened in the presence of water and/or air. The same also applies to so-called inverted structures, in which the light is coupled out of the cathode. In these inverted OLEDs, the anode consists, for example, of Al/Ni/NiOx or Al/Pt/PtOx or other metal/metal oxide combinations which have a highest occupied molecular orbital (HOMO) having an energy of greater than 5 eV. The cathode here consists of the same materials described in points 9 and 10, with the difference that the metal, such as, for example, Ca, Ba, Mg, Al, In, etc., is very thin and thus transparent. The layer thickness is less than 50 nm, better less than

30 nm, still better less than 10 nm. A further transparent material, for example ITO (indium-tin oxide), IZO (indium-zinc oxide), etc., can also be applied to this transparent cathode.

5 Depending on the device structure, a plurality of these layers may also coincide or each of these layers does not necessarily have to be present.

10 However, there are still considerable problems which require urgent improvement:

1. For example, in particular, the OPERATING LIFETIME of OLEDs is still short, meaning that it has hitherto only been possible to implement simple applications commercially.
2. This relatively short lifetime gives rise to a secondary problem: especially for FULL-COLOUR applications ("full-colour displays"), i.e. displays which have no segmentation, but instead are able to display all colours over the entire area, it is particularly unfavourable if the individual colours age at different rates here, as is currently the case. This results in a significant shift in the white point before the end of the above-mentioned lifetime (which is generally defined by a drop to 50% of the initial luminance), i.e. the colour fidelity of the representation in the display becomes very poor. In order to circumvent this, some display users define the lifetime as 70% or 90% lifetime (i.e. drop in the initial luminance to 70% or to 90% of the initial value). However, this results in the lifetime becoming even shorter.
3. Although the efficiencies, in particular the power efficiency (measured in lm/W), of OLEDs are acceptable, improvements are still also desired here – especially for portable applications.
4. The colour coordinates of OLEDs are not good enough. In particular, the combination of good colour coordinates with high efficiency still has to be improved.
5. The ageing processes are generally accompanied by an increase in the voltage. This effect makes voltage-driven organic electroluminescent devices, for example displays or display elements, difficult or impossible. However, current-driven addressing is more complex and expensive in this very case.
6. Precisely in the case of efficient phosphorescent OLEDs, the requisite operating voltage is quite high and therefore has to be reduced further in order to improve

the power efficiency. This is of major importance, especially for portable applications.

7. The requisite operating current has likewise been reduced in recent years, but still has to be reduced further in order to improve the power efficiency. This is particularly important especially for portable applications.
8. The structure of the OLEDs is complex and expensive due to the multiplicity of organic layers.

The above-mentioned reasons make improvements in the production of OLEDs necessary. In particular, improvements in the area of the matrix and hole-blocking materials are of major importance here.

In phosphorescent OLEDs, a hole-blocking layer (HBL) is usually used after the emitter layer in order to increase the efficiency and lifetime. These device structures are usually optimised in accordance with the criterion of maximum efficiency. BCP (bathocuproin) is frequently used here as hole-blocking material (HBM), with which very good efficiencies are achieved (for example D. F. O'Brien *et al.*, *Appl. Phys. Lett.* **1999**, *74*, 442), but with the major disadvantage that the lifetime of the OLEDs comprising BCP is greatly restricted. T. Tsutsui *et al.* (*Japanese J. Appl. Phys.* **1999**, *38*, L1502) indicate, as the reason for the restricted lifetime, the low stability of BCP, meaning that these devices cannot be used in high-quality display applications. A further hole-blocking material is bis(2-methyl-8-hydroxyquinolato)(4-phenylphenolato)aluminium(III) (BAIq). It has enabled the stability and the lifetime of the devices to be significantly improved, but with the side effect that the quantum efficiency of the devices comprising BAIq is significantly (about 40%) lower than with BCP (T. Watanabe *et al.*, *Proc. SPIE* **2001**, *4105*, 175). Kwong *et al.* (*Appl. Phys. Lett.* **2002**, *81*, 162) thus achieved lifetimes of 10,000 h with tris(phenylpyridyl)iridium(III). However, this device only exhibited an efficiency of only 19 cd/A, which is well behind the prior art. Thus, although good lifetimes are possible with BAIq, it is overall not a satisfactory hole-blocking material since the efficiency achieved is too low.

As also evident from the above-described structure of a phosphorescent OLED, this is very complex since a large number of layers, which in turn consist of many diffe-

rent materials, have to be applied one after the other, which makes the production process of commercial OLEDs very complicated and complex.

It is clearly evident from this description that the hole-blocking materials (HBMs) used to date, such as, for example, BCF or BA_{lq}, result in unsatisfactory side effects. There thus continues to be a demand for hole-blocking materials which result in good efficiencies, but at the same time also in long lifetimes, in OLEDs. Surprisingly, it has now been found that OLEDs which comprise certain classes of material – indicated below – as hole-blocking materials have significant improvements over the prior art. Using these classes of material, it is possible simultaneously to obtain high efficiencies and good lifetimes, which is not possible using materials in accordance with the prior art. In addition, it has been found that an electron-transport layer does not necessarily have to be used with the novel hole-blocking materials, which represents a technological advantage, and that consequently the operating voltages can additionally be significantly reduced, which corresponds to higher power efficiency.

The use of spirobifluorene-containing ketones, imines, phosphine oxides, sulfoxides and sulfones has already been described in DE 10317556.3 and DE 10330761.3.

However, only the use as triplet matrix material is described in greater detail there, so that it is not evident how these compounds could otherwise beneficially be employed.

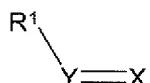
The invention relates to an organic electroluminescent device comprising an anode, a cathode and at least one emission layer comprising at least one matrix material A which is doped with at least one phosphorescent emitter, and at least one hole-blocking layer comprising a hole-blocking material B, characterised in that the hole-blocking material B contains at least one chemical structural unit of the formula Y=X, where X has at least one non-bonding electron pair and where the radical X stands for NR, O, S, Se, Te, and R stands for an organic radical having 1 to 22 carbon atoms and for OH, OR, NH₂, NHR and NR₂, and where the radical Y stands for C, P, As, Sb, Bi, S, Se or Te, with the proviso that the matrix material A is not identical with the hole-blocking material B.

Although evident from the above, it should again explicitly be pointed out here that A and B may contain the same structural unit Y=X, but are otherwise different.

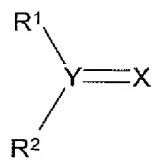
5 The symbol "=" used above and below stands for a double bond in the sense of the Lewis notation of two-electron/two-centre bonds.

10 Preference is given to an organic electroluminescent device which is characterised in that it comprises a hole-blocking material B conforming to the formulae (1) to (4), according to scheme 1,

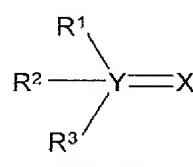
Scheme 1



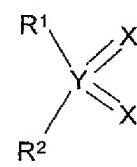
Formula (1)



Formula (2)



Formula (3)



Formula (4)

15 where the symbols used have the following meaning:

Y is equal to C in formula (2) and P, As, Sb, Bi in the formulae (1) and (3) and S, Se, Te in formulae (1), (2) and (4);

X is on each occurrence, identically or differently, NR⁴, O, S, Se or Te;

R¹, R², R³ is on each occurrence, identically or differently, H, F, CN, N(R⁴)₂, a straight-chain, branched or cyclic alkyl, alkoxy or thioalkoxy group having 1 to 40 C atoms, which may be substituted by R⁵ or also unsubstituted, in which one or more non-adjacent -CH₂- groups may be replaced by -R⁶C=CR⁶-, -C≡C-, Si(R⁶)₂, Ge(R⁶)₂, Sn(R⁶)₂, C=O, C=S, C=Se, C=NR⁶, -O-, -S-, -NR⁶- or -CONR⁶- and in which one or more H atoms may be replaced by F, Cl, Br, I, CN or NO₂, or an aromatic or heteroaromatic system or an aryloxy or heteroaryloxy group having 1 to 40 aromatic C atoms, which may be substituted by one or more radicals R⁵, where a plurality of substituents R¹, R² and/or R³ may form a mono- or polycyclic, aliphatic or aromatic ring system with one another; or an aromatic or heteroaromatic ring sys-

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tem bonded via a divalent group $-Z-$, or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may define a further mono- or polycyclic, aliphatic or aromatic ring system, or;

R^4 is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl or alkoxy chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by $-R^6C=CR^6-$, $-C\equiv C-$, $Si(R^6)_2$, $Ge(R^6)_2$, $Sn(R^6)_2$, $-NR^6-$, $-O-$, $-S-$, $-CO-O-$, $-O-CO-O-$ and in which one or more H atoms may be replaced by fluorine, an aryl, heteroaryl or aryloxy group having 1 to 40 C atoms, which may also be substituted by one or more radicals R^6 , or OH or $N(R^5)_2$;

R^5 is on each occurrence, identically or differently, R^4 or CN, $B(R^6)_2$ or $Si(R^6)_3$;

R^6 is on each occurrence, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;

Z is a straight-chain, branched or cyclic, preferably conjugated radical having 1 to 40 C atoms, which is preferably conjugated with the two other substituents, where the number of atoms of Z which link the group of the formula (1) and the aromatic radical is preferably an even number, where one or more non-adjacent C atoms may be replaced by $-O-$, $-S-$ or $-NR^1-$ or one or more C atoms may be substituted by a radical R^1 or halogen;

and with the proviso that the molecular weight of the hole-blocking material B is greater 150 g/mol.

For the purposes of this invention, an aromatic or heteroaromatic system is taken to mean a system which does not necessarily comprise only aromatic or heteroaromatic groups, but instead in which a plurality of aromatic or heteroaromatic groups may also be interrupted by a short, non-aromatic unit, such as, for example, an sp^3 -hybridised C, N, O, etc., atom. Thus, for example, systems such as 9,9'-spirobifluo-

rene, 9,9-diarylfluorene, triarylamine etc., should also be taken to mean aromatic systems for the purposes of this application.

Very particular preference is given to an organic electroluminescent device which is characterised in that Y = C, P or S, and X = O.

It may also be preferred for the hole-blocking material B to contain more than one unit Y=X or more than one unit of the formulae (1) to (4).

The hole-blocking layer preferably comprises at least 50% of the hole-blocking material B, particularly preferably at least 80%, very particularly preferably consists only of the hole-blocking material B.

Particularly suitable hole-blocking materials B have proven to be compounds which do not have a planar structure. Corresponding substituents on the structural unit of the form Y=X may ensure a deviation of the overall structure from planarity. This is the case, in particular, if at least one of the substituents R¹, R², R³ and / or R⁴ contains at least one sp³-hybridised carbon silicon, germanium and / or nitrogen atom which consequently has approximately tetrahedral or, in the case of nitrogen, pyramidal bonding geometry.

In order to achieve a significant deviation from planarity, it is preferred for at least one of the sp³-hybridised atoms to be a secondary, tertiary or quaternary atom, particularly preferably a tertiary or quaternary atom, in the case of carbon, silicon or germanium quaternary atom is very particularly preferred.

A secondary, tertiary or quaternary atom is taken to mean an atom having two, three or four substituents other than hydrogen.

Preference is given to compounds which contain a 9,9'-spirobifluorene derivative, preferably linked via the 2- and / or 2,7- and / or 2,2'- and / or 2,2',7- and / or 2,2'7,7'-position, a 9,9-disubstituted fluorene derivative, preferably linked via the 2- and/or 2,7-position, a 6,6- and/or 12,12-di- or tetrasubstituted indenofluorene derivative, a triptycene derivative, preferably linked via the 9- and/or 10-position, a dihydrophenanthrene derivative, preferably linked via the 2- and/or 2,7-position, a hexaarylben-

zene derivative, preferably linked via the *p*-position on the aromatic ring(s), or a tetraarylmethane derivative, preferably linked via the *p*-position on the aromatic ring(s), in at least one of the radicals R.

5 Particular preference is given to compounds which contain a 9,9'-spirobifluorene derivative in at least one of the radicals R.

The present invention furthermore relates to the use of compounds of the chemical structural unit of the formula Y=X, where X has at least one non-bonding electron pair and where the radical X stands for NR, O, S, Se or Te and R stands for an 10 organic radical having 1 to 22 carbon atoms and for OH, OR, NH₂, NHR and NR₂, where R⁶ = H or an organic radical having 1 to 20 C atoms, and where the radical Y stands for C, P, As, Sb, Bi, S, Se or Te, as hole-blocking material in an organic light-emitting diode.

15 Preference is given to an organic electroluminescent device, characterised in that the matrix materials A are selected from the classes of the carbazoles, for example in accordance with the patent applications WO 00/057676, EP 01/202358 and WO 02/074015, the ketones and imines, for example in accordance with the patent application DE 10317556.3, the phosphine oxides, phosphine sulfides, phosphine

20 selenides, the phosphazenes, the sulfones, the sulfoxides, for example in accordance with the patent application DE 10330761.3, the silanes, the polypodal metal complexes, for example in accordance with the patent application DE 10310887.4, or the oligophenylenes based on spirobifluorenes, for example in accordance with the patent applications EP 676461 and WO 99/40051. Particular preference is given 25 to ketones, phosphine oxides, sulfoxides.

However, this selection is not crucial for the subject-matter of the invention. For example, it is also possible to use further, long-known materials, such as derivatives of carbazole.

30 The OLED described above may also comprise further layers, such as, for example, a hole-injection layer, hole-transport layer, electron-injection layer and/or electron-transport layer. However, it should be pointed out that all these layers do not neces-

sarily have to be present. Thus, it has been found that OLEDs according to the invention which comprise a hole-blocking layer consisting of a hole-blocking material B continue to give comparably good efficiencies and lifetimes at lower operating voltage if no electron-injection and electron-transport layers are used.

6 Preference is likewise given to organic electroluminescent devices which comprise a hole-blocking layer which is directly adjacent to the electron-injection layer or cathode.

10 Preference is furthermore given to an organic electroluminescent device, characterised in that the phosphorescent emitter present is a compound which contains at least one atom having an atomic number of greater than 36 and less than 84.

15 Particular preference is given to an organic electroluminescent device, characterised in that the phosphorescent emitter contains at least one element having an atomic number of greater than 56 and less than 80, very particularly preferably molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold and / or europium, for example in accordance with the patent applications WO 98/01011, US 02/0034656, US 03/0022019, WO 00/70655,

20 WO 01/41512, WO 02/02714, WO 02/15645, EP 1 191613, EP 1 191 612, EP 1 191 614, WO 03/040257 and DE 10215010.9.

25 Preference is furthermore given to an organic electroluminescent device characterised in that the glass temperature T_g of the hole-blocking material B is greater than 100°C, preferably greater than 120°C, very particularly preferably greater than 140°C.

30 Preference is furthermore given to an organic electroluminescent device characterised in that one or more layers are coated by a sublimation process, in which the low-molecular-weight materials are vapour-deposited in vacuum sublimation units at a pressure below 10^{-5} mbar, preferably below 10^{-6} mbar, particularly preferably below 10^{-7} mbar.

Preference is likewise given to an organic electroluminescent device characterised in that one or more layers are coated by the OVPD (organic vapour phase deposition) process or with the aid of carrier-gas sublimation, which are known to the person skilled in the art and in which the low-molecular-weight materials are applied at a pressure between 10^{-5} mbar and 1 bar.

Preference is furthermore given to an organic electroluminescent device characterised in that one or more layers are coated by any desired printing process, such as, for example, flexographic printing or offset printing, particularly preferably LITI (light induced thermal imaging, thermal transfer printing) or ink-jet printing.

The emitting devices described above now have the following surprising advantages over the prior art:

1. The efficiency of corresponding devices is increased compared with systems which do not follow the design according to the invention.
2. The stability of corresponding devices is increased compared with systems which do not follow the design according to the invention.
3. The operating voltages are significantly reduced and consequently the power efficiency is increased. This applies, in particular, if a separate electron-transport layer is not used.
4. The layer structure is simpler since it is possible to use at least one organic layer, namely the electron-transport layer, less, which also has the consequence of lower production complexity. This is a considerable advantage in the production process since in the conventional production process, a separate vapour-deposition unit is generally used for each organic layer, and consequently at least one such unit is thus saved/omitted entirely.

The present application text and also the further examples below are directed only to organic light-emitting diodes and the corresponding displays. In spite of this restriction of the description, it is possible for the person skilled in the art, without further inventive step, also to use the corresponding design according to the invention for other, related devices, for example for organic solar cells (O-SCs), organic field-

effect transistors (O-FETs) or also organic laser diodes (O-lasers), to mention but a few further applications. The present invention likewise relates to these.

Examples:

Production and characterisation of organic electroluminescent devices which correspond to the structure according to the invention.

The OLEDs were produced by the general process outlined below. This had to be adapted in individual cases to the particular circumstances (for example layer-thickness variation in order to achieve optimum efficiency or colour). Electroluminescent devices according to the invention can be produced as described, for example, in the patent application DE10330761.3.

The results for various OLEDs are presented in the following examples. The basic structure, such as the materials and layer thicknesses used, apart from the EMLs and HBLs, were identical for better comparability.

Emitting OLEDs having the following structure were produced analogously to the above-mentioned general process:

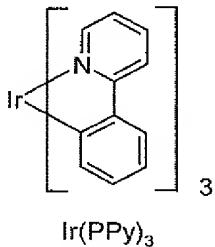
PEDOT (HIL)	60 nm (spin-coated from water; PEDOT purchased from H.C. Starck; poly-[3,4-ethylenedioxy-2,5-thiophene])
NaphDATA (HTM)	20 nm (vapour-deposited; NaphDATA purchased from SynTec; 4,4',4''-tris(N-1-naphthyl-N-phenyl-amino)triphenylamine)
S-TAD (HTM)	20 nm (vapour-deposited; S-TAD prepared as described in WO99/12888; 2,2',7,7'-tetrakis(diphenylamino)spirobifluorene)
Emitter layer (EML)	30 nm (precise structure see examples in Table 1)
Hole-blocking layer (HBL)	10 nm (see examples in Table 1)
AlQ ₃ (ETL)	10 nm (vapour-deposited: AlQ ₃ purchased from SynTec; tris(quinolinato)aluminim(III))
Ba/Al (cathode)	3 nm Ba, 150 nm Al on top

These unoptimised OLEDs were characterised by standard methods; for this purpose, the electroluminescence spectra, the efficiency (measured in cd/A), the power efficiency (measured in lm/W) as a function of the luminance, calculated from

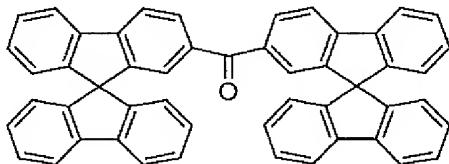
current/voltage/luminance characteristic lines (IUL characteristic lines), and the lifetime were determined. The lifetime is taken to mean the time after which the initial luminance of the OLED, at a constant current density of 10 mA/cm^2 , has dropped to half.

- 5 Table 1 below shows the results for various examples. The composition of the entire
EMLs and HBLs, including the corresponding layer thicknesses, is shown. The
doped phosphorescent EMLs comprise, for example, **A1** the compound bis(9,9'-
spirobifluoren-2-yl) ketone, the compound **A2** bis(9,9'-spirobifluoren-2-yl)phenyl-
phosphine oxide or CBP as matrix material, the compounds Ir(PPy)₃ as emitter, and
10 the compound **B1** bis(9,9'-spirobifluoren-2-yl) ketone or the compound **B2** bis(9,9'-
spirobifluoren-2-yl)phenyl-phosphine oxide as hole-blocking material. OLEDs which
comprise CBP (4,4'-bis(N-carbazolyl)biphenyl) or bis(9,9'-spirobifluoren-2-yl) ketone
as matrix material and B-Alq as hole-blocking material serve as comparative exam-
15 ple.

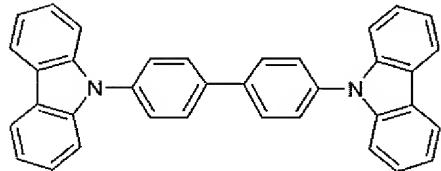
15 The figure below shows the corresponding structural formulae of the substances
shown in the Table.



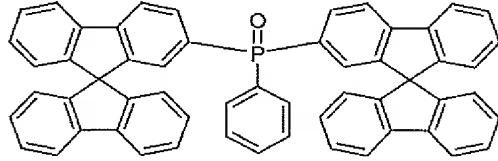
$\text{Ir}(\text{PPy})_3$



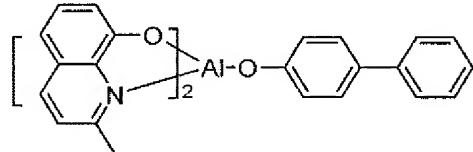
Bis(9,9'-spirobifluoren-2-yl) ketone



CBP



Bis(9,9'-spirobifluoren-2-yl)phenylphosphine oxide



BAIq

Table 1:

Experiment	EML	HBL	ETL	Max. efficiency (cd/A)	Max. power efficiency (lm/W)	Voltage (V) at 100 cd/m ²	Lifetime (h) at 10 mA/cm ²
Example 1a	A1:10% IrPPy	B1 (10 nm)	AlQ ₃ (20 nm)	29.1	16.5	4.7	630
Example 1b	A2:10% IrPPy	B2 (10 nm)	AlQ ₃ (20 nm)	34.0	26.9	4.1	590
Example 1c	CBP:10% IrPPy	B2 (10 nm)	AlQ ₃ (20 nm)	29.7	17.2	4.5	650
Example 1d comparison	CBP:10% IrPPy	BAIq (10 nm)	AlQ ₃ (20 nm)	18.3	8.5	5.1	250
Example 1e comparison	A1:10% IrPPy	BAIq (10 nm)	AlQ ₃ (20 nm)	25.2	14.8	5.7	510
Example 2a	A1:10% IrPPy	B1 (10 nm)	—	30.2	19.1	3.5	710
Example 2b	A2:10% IrPPy	B2 (10 nm)	—	32.7	27.7	3.5	490
Example 2c	CBP:10% IrPPy	B2 (10 nm)	—	27.2	15.9	5.1	330
Example 2d comparison	CBP:10% IrPPy	BAIq (10 nm)	—	16.5	8.8	5.3	180
Example 2e comparison	A1:10% IrPPy	BAIq (10 nm)	—	24.8	14.7	5.2	240

All OLEDs exhibit green emission from the dopant Ir(PPy)₃.

The highest photometric efficiencies are obtained in a device which comprises the matrix material A2, in combination with the HBM B2 (see Example 1b). Since the voltages are also low here, very good power efficiency is also obtained.

5 The use of matrix materials A1 and B1 (see Example 1a) also exhibits a significant improvement over the prior art, a device comprising the matrix material CBP and the HBM Balq (see Example 1d). This is also evident in the corresponding lifetimes, which increase from 250 h to 630 h.

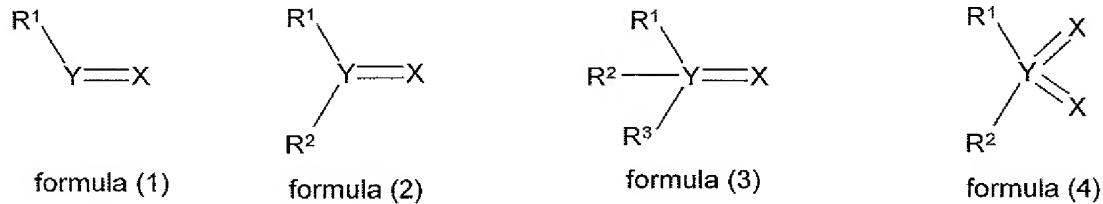
10 A similar trend is evident if the ETL is omitted. In the OLEDs in accordance with the prior art, the photometric efficiency decreases and the lifetime is significantly shortened compared with OLEDs comprising an ETL. This is not the case in the OLEDs manufactured in accordance with the novel design principle, where, in particular, the voltages drop, causing an improvement in the power efficiency. Furthermore, the drop in the lifetime is not as great as in the comparative examples.

15 In summary, it can be stated that OLEDs manufactured in accordance with the novel design principle have higher efficiency at lower voltages and longer lifetimes, as can easily be seen from Table 1.

1. Organic electroluminescent device comprising an anode, a cathode and at least one emission layer comprising at least one matrix material A which is doped with at least one phosphorescent emitter, and at least one hole-blocking layer comprising a hole-blocking material B, characterised in that the hole-blocking material B contains at least one chemical structural unit of the formula $Y=X$, where X has at least one non-bonding electron pair and where the radical X stands for NR, O, S, Se, Te, and R stands for an organic radical having 1 to 22 carbon atoms and for OH, OR, NH₂, NHR and NR₂, where R⁶ = H or an organic radical having 1 to 20 C atoms, and where the radical Y stands for C, P, As, Sb, Bi, S, Se or Te, with the proviso that the matrix material A is not identical with the hole-blocking material B.

2. Organic electroluminescent device, according to Claim 1, characterised in that it comprises a hole-blocking material B conforming to the formulae (1) to (4) according to scheme 1

Scheme 1



where the symbols used have the following meaning:

Y is equal to C in the formula (2) and P, As, Sb, Bi in formula (1) and (3) and S, Se, Te in formule (2) and (4);

X NR⁴, O, S, Se, Te;

R¹, R², R³ is, identically or differently on each occurrence, H, F, CN, N(R⁴)₂, a straight-chain, branched or cyclic alkyl, alkoxy or thioalkoxy group having 1 to 40 C atoms, which may be substituted by R⁵ or also unsubstituted, in which one or more non-adjacent -CH₂- groups may be replaced by -R⁶C=CR⁶-, -C≡C-, Si(R⁶)₂, Ge(R⁶)₂, Sn(R⁶)₂, C=O, C=S, C=Se, C=NR⁶, -O-, -S-, -NR⁶- or -CONR⁶- and in which one or more H atoms may be replaced by F, Cl, Br, I, CN or NO₂, or an

- aromatic or heteroaromatic system or an aryloxy or heteroaryloxy group having 1 to 40 aromatic C atoms, which may be substituted by one or more radicals R⁵, where a plurality of substituents R¹, R² and/or R³ here may form a mono- or polycyclic, aliphatic or aromatic ring system with one another; or an aromatic or heteroaromatic system bonded via a divalent group -Z-, or an aryloxy or heteroaryloxy group, each having 1 to 40 aromatic C atoms, in which one or more H atoms may be replaced by F, Cl, Br or I or which may be substituted by one or more non-aromatic radicals R, where a plurality of substituents R may define a further mono- or polycyclic, aliphatic or aromatic ring system, or;
- 10 R⁴ is on each occurrence, identically or differently, a straight-chain, branched or cyclic alkyl or alkoxy chain having 1 to 22 C atoms, in which, in addition, one or more non-adjacent C atoms may be replaced by -R⁶C=CR⁶-, -C≡C-, Si(R⁶)₂, Ge(R⁶)₂, Sn(R⁶)₂, -NR⁶-, -O-, -S-, -CO-O- or -O-CO-O- and in which one or more H atoms may be replaced by fluorine, an aryl, heteroaryl or aryloxy group having 1 to 40 C atoms, which may also be substituted by one or more radicals R⁶, or OH or N(R⁵)₂;
- 15 R⁵ is on each occurrence, identically or differently, R⁴ or CN, B(R⁶)₂ or Si(R⁶)₃;
- 20 R⁶ is on each occurrence, identically or differently, H or an aliphatic or aromatic hydrocarbon radical having 1 to 20 C atoms;
- 25 Z is a straight-chain, branched or cyclic, preferably conjugated radical having 1 to 40 C atoms, which is preferably conjugated with the two other substituents, where the number of atoms of Z which link the group of the formula (1) and the aromatic radical is preferably an even number, where one or more non-adjacent C atoms may be replaced by -O-, -S- or -NR¹- or one or more C atoms may be substituted by a radical R¹ or halogen;
- 30 and with the proviso that the molecular weight of the hole-blocking material B is greater 150 g/mol.

3. Organic electroluminescent device, according to Claim 1 and/or 2, characterised in that Y = C, P or S, and X = O.

5 4. Organic electroluminescent device, according to one of Claims 1 to 3, characterised in that the hole-blocking layer comprises at least 50% of the hole-blocking material B.

10 5. Organic electroluminescent device, according to Claim 4, characterised in that the hole-blocking layer consists only of the hole-blocking material B.

6. Organic electroluminescent device according to one or more of Claims 1 to 5, characterised in that the compounds of the hole-blocking materials B do not have a planar structure.

15 7. Organic electroluminescent device according to one or more of Claims 1 to 6, characterised in that at least one of the substituents R¹ to R⁴ in the hole-blocking material B contains at least one sp³-hybridised carbon atom.

20 8. Organic electroluminescent device according to Claim 7, characterised in that the sp³-hybridised carbon atom is a secondary, tertiary or quaternary carbon atom.

9. Organic electroluminescent device according to Claim 8, characterised in that the sp³-hybridised carbon atom is a quaternary carbon atom.

25 10. Organic electroluminescent device according to one or more of Claims 1 to 9, characterised in that a 9,9'-spirobifluorene derivative, a 9,9-disubstituted fluorene derivative, an indenofluorene derivative, a triptycene derivative, 9,10-dihydronaphthalene derivative, a hexaarylbenzene derivative or a tetraaryl methane derivative is present in at least one of the radicals R¹ to R⁴.

30 11. Organic electroluminescent device according to one or more of Claims 1 to 10, characterised in that a 9,9'-spirobifluorene derivative is present in at least one of the radicals R¹ to R⁴.

12. Organic electroluminescent device according to one or more of Claims 1 to 11, characterised in that the matrix materials A are selected from the group of the carbazoles, silanes, polypodal metal complexes, oligophenylenes based on spiro-bifluorenes, ketones, imines, phosphine oxides, phosphine sulfides, phosphine selenides, phosphazenes, sulfones, or the sulfoxides.
13. Organic electroluminescent device according to one or more of Claims 1 to 12, characterised in that the hole-blocking layer is directly adjacent to the electron-injection layer or cathode.
14. Organic electroluminescent device according to one or more of Claims 1 to 13, characterised in that the phosphorescent emitter present is a compound which contains at least one atom having an atomic number of greater than 36 and less than 84.
15. Organic electroluminescent device according to Claim 14, characterised in that the phosphorescent emitter contains at least one atom having an atomic number of greater than 56 and less than 80.
16. Organic electroluminescent device according to Claim 14 and/or 15, characterised in that the phosphorescent emitter contains molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, iridium, palladium, platinum, silver, gold and / or europium.
17. Organic electroluminescent device according to one or more of Claims 1 to 13, characterised in that the glass transition temperature T_g of the hole-blocking material B is greater than 100°C.
18. Organic electroluminescent device according to one or more of Claims 1 to 17 characterised in that one or more layers are produced by a sublimation process.

19. Organic electroluminescent device according to one or more of Claims 1 to 18 characterised in that one or more layers are applied by the OVPD (organic vapour phase deposition) process.
- 5 20. Organic electroluminescent device according to one or more of Claims 1 to 18, characterised in that one or more layers are coated by a printing process.
- 10 21. Organic electroluminescent device according to Claim 20 characterised in that one or more layers are coated by the ink-jet printing process.
- 15 22. Organic electroluminescent device according to one or more of Claims 1 to 21, characterised in that one or more layers are coated by the LITI (light induced thermal imaging) process.
- 20 23. Use of compounds of the chemical structural unit of the formula Y=X, where X has at least one non-bonding electron pair and where the radical X stands for NR, O, S, Se or Te and R stands for an organic radical having 1 to 22 carbon atoms and for OH, OR, NH₂, NHR and NR₂, and where the radical Y stands for C, P, As, Sb, Bi, S, Se or Te, as hole-blocking material in an electronic component, in particular in an organic light-emitting diode, organic solar cell, organic field-effect transistor, organic thin-film transistor, organic integrated circuit or organic laser diode.
- 25 24. Organic solar cell, organic field-effect transistor, organic thin-film transistor, organic integrated circuit, organic laser diode, characterised in that the structure complies with one or more of Claims 1 to 22.

Abstract

C03044

Organic electroluminescent element

- 5 The present invention relates to the improvement of phosphorescent organic electroluminescent elements by using materials of the formula (1) to (4) according to Scheme 1 in the hole-blocking layer..